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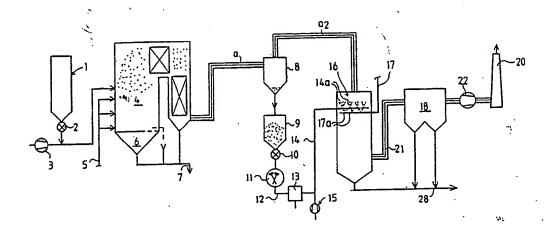
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(54) Title: PROCESS AND EQUIPMENT FOR CLEANING OF FLUE GASES



(57) Abstract

The invention concerns a process for cleaning of flue gases, wherrein a solid material separated from a pre-separator (8) is transferred into an activation device (11) placed after the pre-separator (8), which crushes the pre-separated material particles to smaller particles, whereby the CaSO₄ crust placed around CaO is broken and the CaO is liberated for a hydration reaction. In the process the crushed dust-like material that contains CaO is transferred from the activation device (11) downstream into a reactor (16), which is placed after the flue-gas pre-separator (8) in the direction of flow of the flue gases. In the process the CaO particles are hydrated substantially in the reactor (16) by introducing the CaO particles through nozzles (14a) into a drop zone (A) in the reactor (16), into which zone the water is also introduced through nozzles (17a), whereby the CaO reacts immediately with the water, and the Ca(OH)₂ formed reacts further with the flue gas made to flow in the reactor (16) and binds SO₂ contained in the flue gas. The invention also concerns equipment for cleaning of flue gases.

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Process and equipment for cleaning of flue gases

5 The invention concerns a process and a device for cleaning of flue gases, in which said process an absorption agent is carried into the furnace of a boiler and said agent is reacted with the sulfur contained in the flue gases, the flue gases are carried further out of the furnace of the boiler along an exhaust duct to a pre-separator, which separates any absorption agent unreacted with sulfur from the flue gas and carries said unreacted product into a separate processing unit, wherein the product is activated mechanically.

From the applicant's earlier published Finnish Patent Application

No. 76,931 a process is known wherein the solid material separated from the pre-separator is hydrated and brought into a form reactive with sulfur and transferred downstream into a reactor, which is placed after the flue-gas pre-separator in the direction of flow of the flue gases.

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The object of the invention is an improvement of the above process and in particular of its hydration process. The object is a process and a device by whose means it has been possible to intensify the removal of sulfur out of the flue gases after the furnace of a boiler to a considerable extent.

The object of the invention has been achieved by means of a solution wherein the CaO and CaSo, separated from the flue gases are processed by means of an activation device mechanically, e.g., by crushing,

30 whereby the CaSO, crust surrounding the CaO particles is broken and the CaO is liberated for the hydration reaction. Advantageously, after the activation device, an after-separator is used, wherein the reactive CaO is separated from the other material and from which said after-separator the CaO dust is passed into a reactor in which the hydration proper takes place. The hydrated CaO reacts further with the flue gas introduced into the reactor and binds SO₂ contained in the flue gas efficiently.

In the following, the entire cleaning process will be described step by step.

In the first step, finely ground limestone is blown into the furnace of the boiler to a temperature of 900°C...1200°C, whereby the calcium carbonate is decomposed in accordance with the reaction equation (1):

$$CaCO_3 --- > CaO + CO_2$$
 (1)

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Part of the calcium oxide formed hereby reacts further with sulfur dioxide (2):

$$CaO + SO_2 + 1/2O_2 ----> CaSO_4$$
 (2)

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Thereby calcium sulfate is formed. The proportion of the sulfur that reacts in the furnace may be 10...70 per cent of the overall quantity of sulfur. When an amount of reagent is used that is economically rational in relation to the sulfur contained in the coal, the separation of sulfur taking place in the furnace is thereby about 30...50 % of the total quantity of SO₂. In order that levels lower than the emission limits imposed could be reached, it is mostly necessary to continue the binding of sulfur in a processing taking place after the boiler.

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In the second step of the process, the unreacted CaO and the reaction products are carried along with the flue gases out of the boiler and end up in a pre-separator. As the pre-separator it is possible to use all dry dust separation devices.

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When the particle size of the limestone blown into the furnace has been chosen appropriately in relation to the fly ash, only the fraction that contains mainly CaO ends up in further processing. However, particles of CaO covered with a layer of CaSO₄ also always end up in the further processing, in which case the CaO is activated in accordance with the invention in an activation device, preferably in a press, by crushing the CaSO₄ crust that surrounds the CaO and by

1 liberating the CaO for the hydration reaction.

In the further treatment the separated and ground fraction is hydrated in a reactor in accordance with the following equation.

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$$CaO + H_2O - Ca(OH)_2$$
 (3)

The hydration is indispensable in order that the SO_2 still remaining in the flue gases could be reacted and removed from the gas in accordance with the reaction equation (2).

After the reactor the fly ash and the reaction products are separated from the flue gases. The separator may be, e.g., an electric filter or a hose filter. When a hose filter is used, reaction of binding of sulfur also takes place in the layer of dust formed on the face of the hose.

The process in accordance with the invention is mainly characterized in that the solid material separated from the pre-separator is transferred into an activation device after the pre-separator, which crushes the pre-separated material particles to smaller particles, whereby the CaSO4 crust placed around CaO is broken and the CaO is liberated for the hydration reaction, and in which said process the crushed dust-like material that contains CaO is transferred from the activation device downstream into a reactor, which is placed after the flue-gas pre-separator in the direction αf_i flow of the flue gases, and that in the process the CaO particles are hydrated substantially in the reactor by introducing the CaO particles through nozzles into a drop zone in the reactor, into which zone the water is also introduced through nozzles, whereby the CaO and the water drops can be made to meet in a controlled way, and CaO reacts immediately with water, and the $Ca(OH)_2$ formed reacts further with the flue gas made to flow in the reactor and binds SO_2 contained in the flue gas.

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The equipment in accordance with the invention is mainly characterized in that, after the pre-separator, the equipment

1 comprises an activation device, which crushes the pre-separated material particles to smaller particles, whereby the CaSO₄ crust placed around the CaO is broken and the CaO is liberated for a hydration reaction, the equipment comprising a duct through which the CaO-containing particles are transferred to hydration in a reactor, which is placed after the flue-gas pre-separator in the direction of flow of the flue gases, and said equipment comprising nozzles through which the CaO particles are introduced into the reactor, whereas the water spray nozzles are placed substantially at the proximity of said nozzles.

The invention will be described in the following with reference to some preferred embodiments of the invention illustrated in the figures in the drawing, the invention being, however, not supposed to be confined to said embodiments alone.

Figure 1A shows a press used as an activation device.

Figure 1B is a schematical illustration of the liberation of CaO in the pressing process.

Figures 2 and 3 are schematical illustrations of the process and of the equipment.

In the process for cleaning of flue gases illustrated in Figures 1A to 3, limestone powder is fed into the furnace so that it is first calcinated to calcium oxide (CaO) and then reacts with the sulfur com-pounds contained in the flue gases and forms calcium sulfate (CaSO₄).

$$CaO + SO_2 + 0.5O_2 ----> CaSO_4$$

The proportion of the CaO that participates in the reaction is 5...30 per cent, as a rule 15 per cent. The reason for the low utilization of calcium is the CaSO, crust formed in the reaction, which retards the process of the reaction after a certain layer thickness so that, during the available 0.5...5 s, usually less than

- 2 s, the reaction does not have time to take place. An excessively high temperature, usually < 1150°, causes sintering on the faces of the limestone particles, which deteriorates the reactivity.
- 5 The reaction products and the fly ash are carried along with the flue gases into the sulfur-removing unit after the boiler, wherein the unreacted CaO is first pre-separated.

By means of the process in accordance with the invention, the calcium-containing CaO particle is reactivated by breaking the CaSO₄ crust that surrounds it. This takes place after the pre-separation of the CaO in an activation device, advantageously in a press. The product crushed fine in the activation device is fed into the drop zone in the flue-gas moistening reactor, whereby CaO is hydrated to Ca(OH)₂, which binds SO₂ efficiently and forms calcium sulfite CaSO₃. The feeding of the fine-crushed product takes place, e.g., by means of carrier air so that powdery product is fed through nozzles into the drop zone in the flue-gas moistening reactor. Thus, CaO is hydrated to Ca(OH)₂ substantially in the flue-gas moistening reactor.

Only the particles with the highest contents of calcium oxide CaO are passed to the hydration process, whereas, e.g., the fly ash is separated in an after-separator after the activation device.

- Thus, the following reactions take place in the drop zone in the flue-gas moistening reactor: CaO is hydrated to $Ca(OH)_2$, and $Ca(OH)_2$ reacts with the sulfur oxide SO_2 contained in the flue gas and forms calcium sulfite $CaSO_3$.
- 30 Besides producing the hydration process, the flue gases are also cooled by means of the water sprayed into the drop zone in the flue-gas moistening reactor.
- Fig. 1A illustrates an activation device 11 in accordance with the invention, which is preferably a press. From the pre-separator the pre-separated CaO-containing material flow J is passed into the press 11, where it is carried between press disks E₁ and E₂ while the

1 revolving disks E_1, E_2 pull material into the space between the disks E_1, E_2 , the material being subjected to intensive compression.

Fig. 1B illustrates a CaO particle, which is surrounded by a $CaSO_4$ crust, the crust retarding the hydration of CaO in the hydration reaction substantially. According to the invention, this $CaSO_4$ crust is broken by pressing the CaO-CaSO₄ particle between the mechanical press disks E_1, E_2 . At the CaO-CaSO₄ interface fracture lines F_1, F_2, F_3 are formed, and $CaSO_4$ is detached along the interface from the face of the CaO component, whereby CaO is liberated for the hydration reaction.

In Fig. 2, the silo for the absorption agent, preferably limestone, is denoted with the reference numeral 1. In the bottom part of the 15 silo there is a dosage device 2 for the absorption agent. The transfer air blower 3 blows the carrier air, in which the absorption agent is mixed, into the furnace of the boiler 4. The combustion air and the coal are introduced along the ducts 5. In the preferred embodiment the boiler is a dust-burning boiler. But such an embodi-20 ment is also possible wherein the boiler is a so-called gratefurnace boiler or a combined grate-furnace/dust-burning boiler, in which case the grate is denoted with the reference numeral 6 (as in the figure). The slag is removed from the boiler along the duct 7. The flue gases are passed out of the boiler construction along the 25 flue-gas duct a into the flue-gas pre-separator 8. In the preferred embodiment the pre-separator 8 consists of a cyclone. The sorted particles are separated into an intermediate silo 9. The closing device 10, which is advantageously a so-called closing feeder, distributes the fraction, which has entered from the pre-separator 8 30 into the intermediate silo 9, into the activation device 11, preferably a press. From the reactor 16 the flue gas is passed along the duct 21 into the dust separation device 18. The dust separation device may comprise an electric filter or a hose filter device for separation of the dust. The flue-gas blower 19 sucks the flue gas 35 out of the dust separation device 18 and blows it into the chimney 20 and from there further into the open air. From the units 16 and 18 the separated flue-gas impurities, e.g. CaSO₄, are removed along

the exhaust line 28.

In the activation device 11 the sintered pre-separated CaO and the CaSO4 particles are processed mechanically, the CaO particle being reactivated by breaking the CaSO4 crust surrounding the CaO, so that the CaO is liberated for hydration. From the activation device 11 the activated particle is carried along the duct 12 into the afterseparator 13 and along the duct 14 into the reactor 16. Carrier air or carrier gas is supplied into the duct 14 by means of a blower arrangement 15. The material can also be passed from the activation 10 device 11 directly into the reactor 16, in which case no afterseparator 13 is used. The dust-like activated CaO-containing material is sprayed through the nozzle 14a into the drop zone A in the reactor 16. The water is also atomized into the drop zone A in 15 the reactor 16, said water producing hydration of CaO into Ca(OH)2. A second purpose of the supply of water is cooling of the flue gases. The hydrated CaO reacts, in the form of Ca(OH)2, efficiently with the SO_2 contained in the flue gases and forms calcium sulfite $CaSO_3$. The water is passed along the duct 17 and atomized as drops 20 through the end nozzles 17a of the duct 17 into the reactor 16. The end nozzles 17a are placed right next to the dust nozzles 14a, so that direct contact and reaction between the constituents participating in the hydration reaction are ensured.

25 The reactive CaO dust separated from the flue-gas flow is passed efficiently into the area of the water mist A in the reactor 16, so that a good water/solids contact is ensured. The flue gas is made to flow in the reactor 16 so that the flue gas and the Ca(OH)₂ particles formed on hydration meet one another as efficiently as possible.

30 Thereby good contact of Ca(OH)₂ particles with the SO₂ contained in the flue gas is ensured. The directions of introduction of the CaO-containing dust and of water out of their nozzles 14a,17b are favourably perpendicular to the direction of flow (S) of the flue gas.

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The supply of water and dust can be carried out in a concentrated way to the centre of the reactor 16 so that the walls of the reactor

remain dry.

Water is fed through the nozzles 17a so that the heat contained in the flue gases has time to evaporate all the water and that wet 5 solids suspension or waste water is not formed at any stage.

Fig. 3 is a more detailed illustration of the process and equipment in accordance with the invention. When the CaO-CaSO, mixture is processed mechanically by means of the activation device 11, e.g. a 10 press, mill, grinder, crusher, the CaSO4 crust surrounding the CaO is broken so that CaO is liberated for hydration. In the way shown in Fig. 2, the mechanically processed ${\rm CaO}$ and ${\rm CaSO_4}$ are passed further along the duct 12 into the after-separator 13. In the afterseparator 13 classification takes place, by means of which it is possible to separate fly ash or CaSO4 from the active CaO dust flow, 15 and thereby it is possible to reduce the flust load of the reactor 16 and the dust load of the dust separation device after the reactor 16. As is shown in Fig. 3, the processed activated dust-like CaO material is fed through the nozzle 14a in the duct 14 into the fluegas flow S in the reactor 16, and said feeding takes place into the 20 drop zone A in the flue-gas reactor, at the same time with the water mist D fed into the drop zone A out of the nozzles 17a. The water mist D is introduced out of the nozzles 17a in the duct 17. The nozzles 17a are placed in the drop zone A of the reactor 16 at the proximity of the dust nozzles. The drop zone A means the area inside 25 the reactor 16 in which the atomized water $\mathrm{H}_2\mathrm{O}$ has not yet been vaporized by the effect of the thermal energy transferred from the flue gas S.

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CLAIMS:

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- 1. Process for cleaning of flue gases, wherein an absorption agent is carried into the furnace of a boiler (4) and said agent is reacted with the sulfur contained in the flue gases, and wherein the flue gases are carried further out of the furnace of the boiler along an exhaust duct (a) to a pre-separator (8), which separates any absorption agent unreacted with sulfur from the flue gas as well as part of the particles of absorption agent that have already reacted with the sulfur contained in the flue gas, charac t e r i z e d in that the solid material separated from the preseparator (8) is transferred into an activation device (11) placed after the pre-separator (8), which crushes the pre-separated material particles to smaller particles, whereby the $CaSO_4$ crust placed around CaO is broken and the CaO is liberated for a hydration 15 reaction, and in which said process the crushed dust-like material that contains CaO is transferred from the activation device (11) downstream into a reactor (16), which is placed after the flue-gas pre-separator (8) in the direction of flow of the flue gases, and that in the process the CaO particles are hydrated substantially in 20 the reactor (16) by introducing the CaO particles through nozzles (14a) into a drop zone (A) in the reactor (16), into which zone the water is also introduced through nozzles (17a), whereby the CaO and the water drops can be made to meet in a controlled way, and CaO reacts immediately with the water, and the Ca(OH)2 formed reacts 25 further with the flue gas made to flow in the reactor (16) and binds SO_2 contained in the flue gas.
- 2. Process as claimed in claim 1, c h a r a c t e r i z e d in 30 that, before the CaO-containing material crushed in the activation device (11) is transferred into the reactor (16), the constituents with the highest contents of CaO are separated in an after-separator (13) placed after the activation device (11) and transferred into the reactor (16).

3. Process as claimed in claim 1 or 2, $\,$ c h a r a c t e r i z e d in that the dust-like CaO-containing material is brought into the

- reactor (16) along with carrier air or carrier gas.
 - 4. Process as claimed in any of the preceding claims, c h a r a c t e r i z e d in that the hydration is started before the reactor (16) by feeding steam or water into the CaO-containing material flow after the activation device (11).
- 5. Process as claimed in any of the preceding claims, c h a r a c t e r i z e d in that the CaO-containing dust-like material is fed into a drop zone (A) in the reactor (16) into the central area in the reactor (16), and it is made to flow out of the nozzles in such a way towards the flue gas (S) that the directions of flow and the velocities of the flue gas and the dust are optimal in view of obtaining a good contact between the reactive substances.

- 6. Process as claimed in any of the preceding claims, c h a r a c t e r i z e d in that the water is sprayed out of nozzles (17a) which are placed right at the side of the dust nozzles (14a), whereby an optimal contact between the reactive constituents is permitted, and that the water and the CaO-containing dust are sprayed in such a way that their directions of flow are substantially contrary to the direction of flow (S) of the flue gas.
- 7. Process as claimed in any of the preceding claims, c h a r a c 25 t e r i z e d in that in the method a mechanical activation device, preferably a press, is used as the activation device (11).
- 8. Equipment for cleaning of flue gases, comprising a flue-gas duct
 (a) passing out of the furnace of the boiler (4) and therein a

 30 branch point to a pre-separator (8), which separates the absorption agent that has been fed into the furnace of the boiler (4) but has not reacted with sulfur from the flue gas as well as, also, part of the particles of absorption agent that have already reacted with the sulfur contained in the flue gas, c h a r a c t e r i z e d in

 35 that, after the pre-separator (8), the equipment comprises an activation device (11), which crushes the pre-separated material particles to smaller particles, whereby the CaSO4 crust placed around

- the CaO is broken and the CaO is liberated for a hydration reaction, the equipment comprising a duct (14) through which the CaO-containing particles are transferred to hydration in a reactor (16), which is placed after the flue-gas pre-separator (8) in the
- 5 direction of flow of the flue gases, and said equipment comprising nozzles (14a) through which the CaO particles are introduced into the reactor (16), whereas the water spray nozzles (17a) are placed substantially at the proximity of said nozzles (14a).
- 9. Equipment as claimed in claim 8, c h a r a c t e r i z e d in that the equipment comprises an after-separator (13) between the activation device (11) and the reactor (16), in which case only the particles with the highest contents of CaO are transferred into the reactor (16).

10. Equipment as claimed in any of the preceding claims 8 or 9, c h a r a c t e r i z e d in that the equipment comprises a blower (15) or equivalent, by whose means a flow of carrier air is produced

into the material fraction transferred along the duct (14).

11. Equipment as claimed in any of the preceding claims 8, 9 or 10, c h a r a c t e r i z e d in that the activation device (11) consists of a press.

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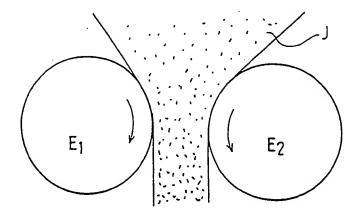


FIG.1A

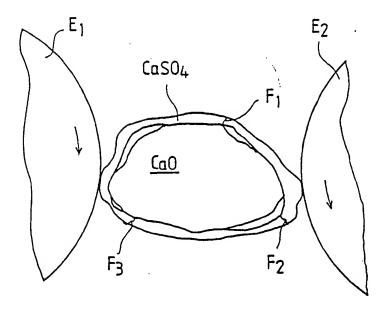
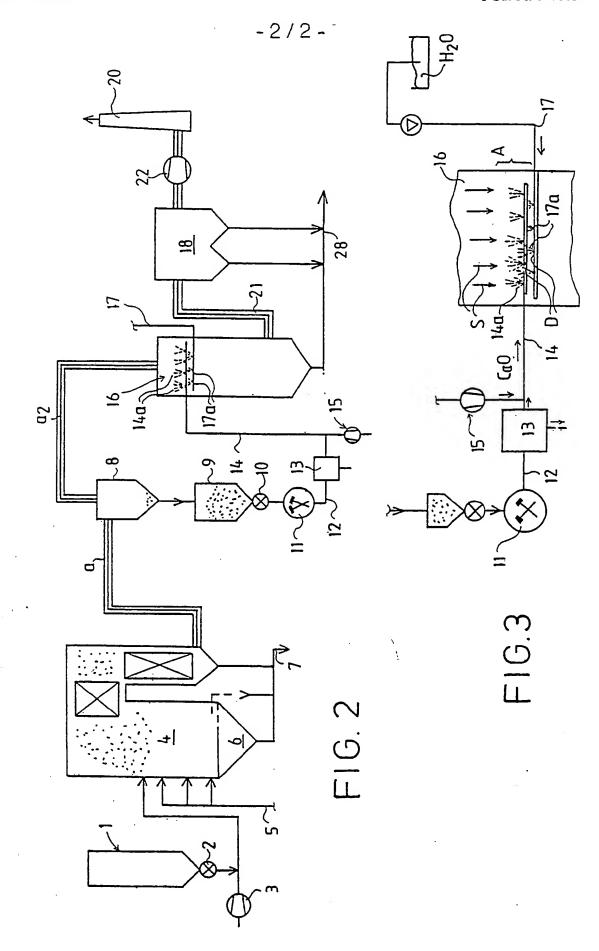


FIG.1B



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INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 90/08037

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶							
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 90-03-30. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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